Chromia–chrominum phosphates as solid acid catalysts

Yu-Wen Chen [1] and Chiuping Li [2]

Department of Chemical Engineering, National Central University, Chung-Li 32054, Taiwan, ROC

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A series of chromia–chrominum phosphate catalysts with various P/Cr ratios were prepared with the coprecipitation method. The surface acidic properties of these catalysts were examined by temperature-programmed desorption (TPD) of ammonia and the dehydration reaction of isopropanol. The dehydration reaction was carried out in a continuous-flow microreactor at 220°C under atmospheric pressure. The results of TPD of ammonia indicated that the surface acidity of chromia–chrominum phosphate is medium strong. The acidic strengths are approximately the same for all the samples. However, the acid concentration is increased with increasing the P/Cr ratio of the catalyst. The dehydration activity of the catalyst is also increased with increasing the P/Cr ratio of the sample. The results indicated that the addition of phosphorus on chromia, even in a small amount, could significantly enhance the acidities of the catalysts. In addition, the acid amount of mixed oxide is decreased in the order: iron oxide–iron phosphate > chromia–chrominum phosphate > alumina–aluminum phosphate.

Keywords: Chromia–chrominum phosphate; isopropanol dehydration; solid acid catalyst; characterization (temperature-programmed desorption of ammonia)

1. Introduction

The applications of binary oxides such as silica–alumina, alumina–aluminum phosphate, alumina–aluminum borate, and iron oxide–iron phosphate, to catalyze the dehydration, isomerization, and alkylation have been widely reported in recent years [1–11]. One important result of the reported mixed-oxide work is the knowledge that some of these materials can function as strong solid acids, some even behaving as superacids [8]. Recent work has shown that the surface acidities are affected by the exact stoichiometry of the mixed oxide [2–5].

Here, we report a study of acidic properties of chromia–chrominum phosphates (CrPs) as determined by temperature-programmed desorption of ammo-

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[1] To whom all correspondence should be addressed.

[2] Present address: Refining and Manufacturing Research Center, Chinese Petroleum Corporation, Chia-Yi, Taiwan, ROC.

nia. We also studied the dehydration reaction of isopropanol in order to understand the correlation with the acidic properties. Of particular interest was the relation between the acidities and their compositions. Previous reported results of the acidities of iron oxide–iron phosphates and alumina–aluminum phosphates [4] are also included just for comparison.

2. Experimental

2.1. CATALYST PREPARATION

Chromia–chrominum phosphates were prepared by the coprecipitation method. An acidic solution was prepared by dissolving chrominum nitrate (Merck) in distilled water and then adding phosphoric acid (Merck) in a suitable amount. A second solution was prepared using a 1:1 volume mixture of ammonium hydroxide and distilled water. The two solutions were slowly added into a container of distilled water with the rate of addition controlled in order to maintain a constant pH of 8.00 ± 0.02 throughout the precipitation process. After the addition of the acidic solution was completed, the reaction mixture was stirred for an additional 10 min. The resulting precipitate was then filtered, washed with distilled water and dried overnight at 120°C. The oven-dried material was calcined at 500°C in a muffle furnace for 12 h. The samples were stored in a desiccator and used without further pretreatment, unless otherwise specified. The P to Cr ratios were obtained by inductively coupled plasma-atomic emission spectrophotometer (Herarus CHN-O-Rapid). Materials were first dissolved in aqua regia and then diluted to a concentration of about 1000 ppm for measurement. The P/Cr ratios of the precipitates were the same as those of starting materials within experimental error ($\pm 2\%$). The specific surface areas and pore volumes of these samples were determined by adsorption of nitrogen at -197°C using a Micromeririics 2600 surface area analyzer.

2.2. NH_3 TPD

In a typical experiment, 100 mg of sample in a U-shaped quartz tube was activated with He at 300°C for 3 h. After cooling to room temperature, high purity ammonia (99.99%) was adsorbed. The temperature was raised and held at 120°C until no physically adsorbed NH_3 was desorbed. The temperature was then automatically raised at 5°C/min to 700°C under a stream of He at 30 ml/min. Ammonia desorbed from the sample was trapped in a buffer solution of boric acid and autotitrated with sulfamic acid using the Radiometer RTS822 automatic titrator. The total acid amount of the sample can be read in the automatic titrator.

2.3. ISOPROPANOL DEHYDRATION

The catalytic activities of these samples were investigated using isopropanol dehydration as a test reaction. In a typical experiment 100 mg of sample, fixed with 200 mg quartz wool in a U-tube pyrex reactor, was reactivated at 300°C for 3 h. A saturator containing the isopropanol was kept at a 25°C. Nitrogen carrier gas flowed at a constant flow rate of 30 ml/min. The temperature in the furnace containing the reactor could be controlled to within ±0.1°C. A thermocouple located in the thermowell of the reactor confirmed isothermal operation. Several millimeters of glass wool were placed at each end of the reactor to avoid entrance and exit effects. The product was sampled by a six-port valve and analyzed by a Shimadzu gas chromatograph (GC-8A) with a thermal conductivity detector. The column was 3 m long and packed with 5% Carbowax in 60–100 mesh HMDS-treated acid-washed Chromsorb W at 50°C. To prevent condensation of reactants and products, all connections from the saturator to the chromatograph were heated by heating tapes at 50°C. The steady state data for each run were taken 4 h time-on-stream. The precision or repeatability of the conversion data was ±3%.

Calibration samples were prepared and used in converting detector response to concentrations. Reaction products were identified by comparing their retention times with those of standards. Quantitative analysis was accomplished by comparing the peak areas of each sample with those of the standard.

3. Results and discussion

3.1. NH_3 TPD

The acidities of chromia–chrominum phosphates with various P/Cr ratios were measured by the temperature-programmed desorption (TPD) of ammonia. The ammonia desorption temperature and the amount of ammonia evolved are considered to be an index of acid strength and acid amount, respectively [12]. Fig. 1 shows that the maximum desorption temperatures (T_{max}) of CrPs with various P/Cr ratios are 280°C, indicating intermediate acid strengths. The acid strengths of CrP catalysts are much greater than that of chromia. In addition, they are independent of the P/Cr ratios of the catalysts. Fig. 2 demonstrates that the total acid amount is closely related to the P/Cr atomic ratio of CrP catalyst. Campelo et al. [13] reported that the surface acidity of alumina–aluminum phosphate is determined by the degree of crystallinity and P/Al ratio. The higher the P/Al atomic ratio, the greater the acid strength. Wendt and Lindstrom [14] obtained the same results. In this study, we found that the acid amount of CrP increased with increasing P/Cr atomic ratio. However, this composition effect has no influence on the acidic strength. The other important

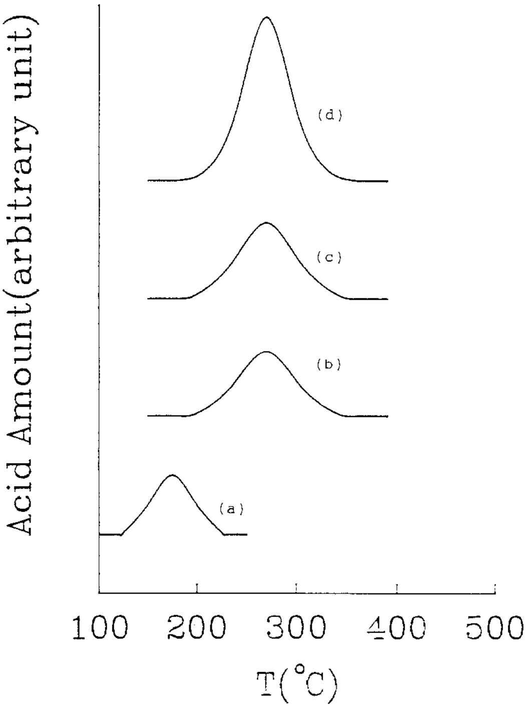

Fig. 1. NH_3 TPD of chromia-chrominum phosphate catalysts. (a) P/Cr atomic ratio = 0, (b) P/Cr = 0.05, (c) P/Cr = 0.33, (d) P/Cr = 1.0.

information that can be extracted from the TPD spectra is the lack of bimodal distribution as would be expected for materials consisting of simply a mixture of two oxides. This result indicates that these materials are not just mixtures of chromia and chrominum phosphate. To be more specific, the monodisperse distribution of TPR spectra of CrP implies that it is a true microcomposite structure material rather than a mixture of the individual materials.

In order to determine the effect of metal cation on the acidities of metal phosphates, previous reported results of the acidities of alumina-aluminum phosphates (AlPs) and iron oxide-iron phosphates (FePs) are plotted in fig. 3 for comparison. Fig. 3 demonstrates that the acid amounts of CrP, FeP, and AlP all increase with increasing phosphorus content. In addition, the acid amount decreases in the order: FeP > CrP > AlP.

3.2. ELIMINATION OF EXTERNAL AND INTERNAL MASS TRANSFER RESISTANCE

Prior to any kinetic measurements, it is essential to ensure that mass transport processes do not influence the observed reaction rates. Thus, preliminary experiments were conducted with various flow rates and catalyst particle sizes, in order to establish the reaction conditions which would eliminate the film and

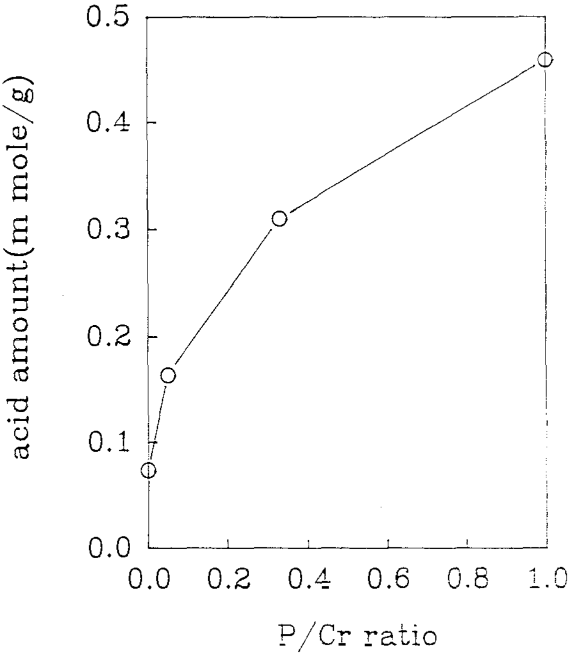

Fig. 2. Acid amount versus P/Cr atomic ratio for chromia-chrominum phosphate catalysts.

intraparticle diffusion resistances, respectively. From these preliminary experiments it was determined that a gas hourly space velocity of 1200 was more than sufficient to eliminate film resistances from influencing the observed reaction

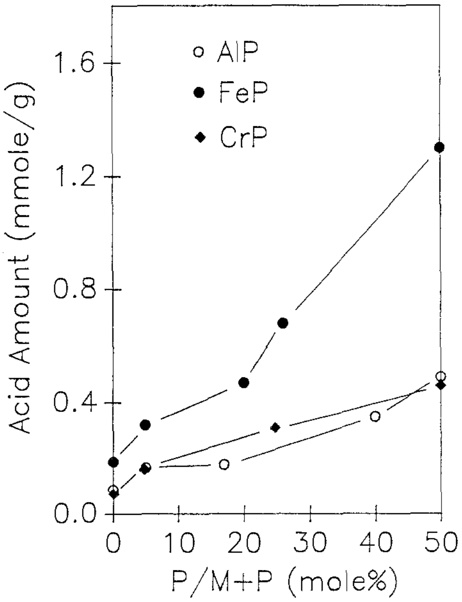

Fig. 3. Acid amount versus phosphorus content.

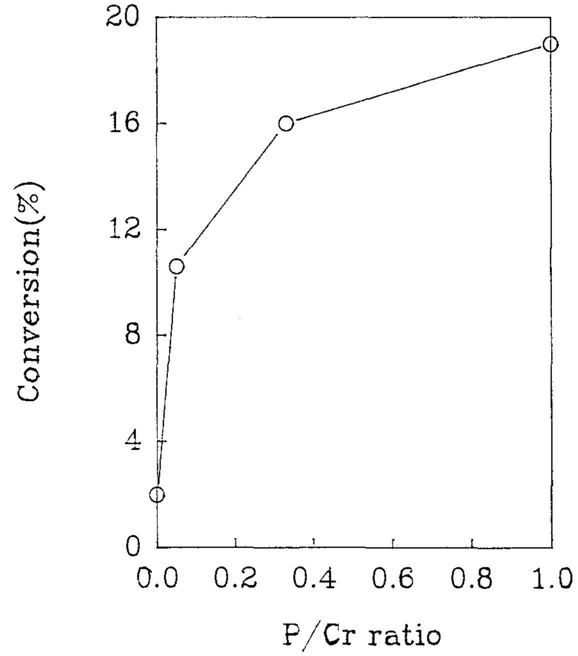

Fig. 4. Isopropanol dehydration activity versus P/Cr atomic ratio for chromia-chrominum phosphate catalysts. (Reaction temperature: 220°C.)

rates. Similarly, it was determined that catalyst particles with an average diameter of 90 μm were sufficient to eliminate intraparticle diffusional resistances from influencing the observed reaction rates. All reaction experiments were conducted with a GHSV of 1200, while the catalyst particles did not exceed 90 μm in diameter.

3.3. ISOPROPANOL DEHYDRATION REACTION

In the isopropanol catalytic reaction, there are three possibilities: (i) monomolecular dehydration to propylene and water, (ii) dehydrogenation to ketone and hydrogen, and (iii) bimolecular dehydration to diisopropyl ether and water. The results of this study indicated that isopropanol proceeds simply the monomolecular dehydration reaction to propylene and water on CrP catalysts. Only trace amounts of other products were detected. Fig. 4 shows the dehydration activities of CrP catalysts are a function of P/Cr atomic ratio. This can be attributed to the number of the acidic sites, not by the acid strength, since all CrP catalysts have the same acid strength. Murakami et al. [15] also obtained the same results in the acidic cracking reaction over alumina-aluminum phosphate catalysts. The increase in the phosphorus content can elevate the concentration of acidic sites, and this would result in the increase of dehydration activities. Peil et al. [9] concluded that the dehydration of isopropanol is not a very demanding reaction when it comes to acid strength. Even in pure Cr_2O_3 some activity for dehydration of isopropanol is evident at 180°C. The high catalytic acidity of CrP catalyst is also evident from the relatively high conversion of isopropanol at 220°C. The temperatures normally reported in the literature [9–16] for secondary alcohol dehydration range from 250 to 350°C.

4. Conclusion

A series of chromia–chrominum phosphate catalysts with various P/Cr ratios have been prepared via the precipiation technique. TPD of NH_3 and isopropanol dehydration reaction have been used to characterize the surface acidities of these catalysts. TPD of NH_3 results indicated that CrP catalysts belong to medium strength acids. The amount of acid sites is increased with increasing the P/Cr ratio. In addition, the activity of isopropanol on CrP is increased with increasing the P/Cr ratio of the catalyst. This is essentially due to the different concentration of acidic sites, not to the acidic strengths of these catalysts. The addition of phosphorus on chromia, even in a small amount, can significantly enhance the acidities of the catalysts. In adition, the acid concentration of mixed oxide is decreased in the order: FeP > CrP > AlP.

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References

[1] K. Tanabe, *Solid Acids and Bases* (Academic Press, New York, 1970).
[2] J.B. Moffat, Catal. Rev. Sci. Eng. 18 (1978) 199.
[3] S.F. Mitchell, G. Marcelin and J.G. Goodwin Jr., J. Catal. 105 (1987) 521.
[4] Y.W. Chen, P.Z. Wang and W.J. Wang, Catal. Lett. 6 (1990) 187.
[5] W.J. Wang and Y.W. Chen, Catal. Lett. 10 (1991) 297.
[6] B.C. Gates, J.R. Katzer and G.C. Schuit, *Chemistry of Catalytic Process* (McGraw-Hill, New York, 1979).
[7] L.A. Pine, US Patent 3,993,557 (1976).
[8] S. Sato, S. Hasebe, H. Sakurai, K. Urabe and Y. Izumi, Appl. Catal. 29 (1987) 107.
[9] K. Peil, L.G. Galya and G. Marcelin, J. Catal. 115 (1989) 441.
[10] G. Marcelin, R.F. Vogel and W.L. Kehl, Appl. Catal. 12 (1984) 237.
[11] O.V. Krylov, *Catalysis by Nonmetals* (Academic Press, New York, 1970).
[12] F. Delanny, *Characterization of Heterogeneous Catalysts* (Dekker, New York, 1984).
[13] J.M. Campelo, J.M. Marinas, S. Mendioroz and J.A. Pajares, J. Catal. 101 (1986) 484.
[14] G. Wendt and C.F. Lindstrom, Z. Chem. 12 (1976) 500.
[15] Y. Murakami, H. Nozaki and J. Turkevich, Shokubai 5 (1963) 262.
[16] C.L. Kibby and W.K. Hall, J. Catal. 29 (1973) 144.